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Ion exchange uptake of ammonium in wastewater from a Sewage Treatment Plant by zeolitic materials from fly ash

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ABSTRACT

The potential value of zeolitic materials (ZM) obtained from a hazardous waste, such as coal fly ash, for the retention of NH_4^+ present in liquid effluents from a Sewage Treatment Plant (STP) is studied. A wastewater sample was taken from an STP in Zaragoza (Spain) after conventional treatment at the Plant. The water was treated with different amounts of three ZM: NaP1 zeolite, K-F zeolite and K-Chabazite/K-Phillipsite zeolites all of them in powdered and granulated state. The wastewater was treated by two kinds of processes: continuous stirring batch experiments with powdered ZM, and fixed packed bed of granulated ZM in a column. The powdered materials reduced about 80% of NH_4^+ from wastewater, even in the presence of Ca^{2+}, which competes with NH_4^+ for the cation exchange sites in zeolites. Around 70% of NH_4^+ reduction was achieved with granulated materials. In both cases, moderate ZM/wastewater ratios had to be used to achieve those results, with K-zeolites slightly less effective in NH_4^+ retention.

1. Introduction

Urban wastewaters usually contain a considerable amount of ammonium (NH_4^+), which is mostly removed using conventional methods such as activated sludge process, including flocculation and active carbon treatment. However, although the remaining NH_4^+ concentration after treatment is low (about 30–50 ppm), it becomes an environmental problem if discharged into a waterway with low water flow, as ammonium can encourage eutrophication of the waters receiving the discharge. This is potentially toxic for fish and other aquatic life, particularly if that water flows through a sensitive area, as was noted in some publications [1,2]. As the discharge of effluent waters containing ammonia and ammonium is coming under increasingly strict concentration limits discharge and the quality of water intended for human consumption as seen in the Directives from the Council of the European Union [3,4], the recommendation of American Committee on Water Quality [5] and discharge standards in some countries such as New Zealand [1], it will be necessary to comply with the requirements for wastewater treatment in a way that minimizes its impact on the environment. In some cases, it would be necessary to incorporate additional treatment, e.g. ion exchange with materials such as zeolites, given that they may be effective agents in the process of reducing NH_4^+ concentration.

Zeolites are naturally occurring, hydrated aluminium-silicate minerals with cation exchange capacity and affinity for NH_4^+, as has been demonstrated in studies with natural zeolites, such as clinoptilolite, K-Chabazite or K-Phillipsite. This shows potential usefulness for removing this contaminant in wastewaters of different origins – urban, industrial or agricultural – as has been shown in different studies [1,2,6–10].

Over the last decade, intensive research has been focused on the use of coal fly ash for zeolite synthesis [11–14], and the application of the resulting ZM in the same way as natural zeolites, i.e. cation exchangers for of NH_4^+ and heavy metal removal, as reported by different authors [15–19]. However, in most of these studies, application was exclusively tested on synthetic solutions of those ions prepared in laboratories. Considering the complexity of the effluents to be treated in real cases, cation removal with zeolites that do not exhibit comparably high cation selectiveness could be limited when applied to real wastewater samples.

The present study deals with the application of three zeolitic materials (one Na- and two K-zeolites) obtained from coal fly ash, to the treatment of urban wastewater, after conventional treatment at a Sewage Treatment Plant (STP) and before discharge into the Ebro river (Zaragoza, Spain). The main objective of this work is to evaluate the effectiveness of those ZM as water purification agents in environmental protection through their ammonium exchange capacity. The influence of zeolite type, grain size and

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zeolite/wastewater ratio on the wastewater treatment has been studied.

2. Materials and methods

2.1. Zeolitic materials

Three ZM, each containing a NaP1 zeolite, a K-F zeolite, and a K-Phillipsite/K-Chabazite mixture, respectively, were synthesised from coarse and fine fractions of the by-product from manufacture of a lightweight aggregate (LA) made from coal fly ash agglomerated with lime. Synthesis was by means of alkali hydrothermal treatment using the same reaction conditions as previously described [20] and shown in Table 1. These ZM were used to evaluate their ability to remove NH_4^+ from urban wastewater. Treatment tests in batch process (shaking a fixed quantity of ZM with a fixed volume of wastewater) and column (flow-through) with the aforementioned wastewater were performed at room temperature (about 25 °C). Two different fractions of ZM presenting different particle sizes (d) were used: fine ZM ($d < 0.2$ mm) for batch experiments, and coarse ZM ($0.8\ \text{mm} \geq d \geq 0.2$ mm) for column experiments. The size range for that last fraction of ZM has been proven to be suitable for work in laboratory as bed load in ion exchange columns. The size range of that fraction does not lead to a pressure deeping in stream due to partial plugging of the bed support in the column.

Cation exchange capacities (CEC) of coarse and fine zeolitic products were determined by NH_4^+ exchange. For CEC determinations of fine ZM, 50 ml of NH_4NO_3 solution, containing 0.35 eq NH_4^+/l, was mixed at room temperature with 0.5 g of each ZM. After continuous stirring for 30 min (this is the time required for NH_4^+ exchange equilibrium with the cited ZM to be achieved, as found in previous studies [20]), the mixture was filtered and the solid residue was washed with deionized water until remaining NH_4^+ was removed (test with Nessler's reagent was used) and dried at room temperature. After that, the exchanged NH_4^+ is extracted from the solid with 50 ml of a solution containing 0.35 eq/l of Na^+ ($NaNO_3$ for NaP1 zeolite) or K^+ (KNO_3 for K-zeolites). NH_4^+ concentration in the solution was determined by colourimetry ($\lambda = 410$ nm) using Nessler's method [21].

For determining the coarse ZM CEC, 50 ml of NH_4NO_3 solution containing 0.35 eq NH_4^+/l was passed at room temperature through 0.5 g of each ZM in a packed bed (equivalent to 1 cm bed height) in a glass column of 1 cm inner diameter. The feed was introduced using a peristaltic pump at volumetric flow of 0.35 ml/min. A low flow rate was chosen to ensure an adequate contact time for ZM-solution in order to achieve saturation in those conditions. After the 50 ml of ammonium salt were passed, the column was washed with 500 ml of deionized water to remove residual NH_4^+. The NH_4^+ in the ZM was then extracted by passing 50 ml of a solution containing 0.35 eq/l of Na^+ ($NaNO_3$) or K^+ (KNO_3) through the NH_4-ZM bed. Finally, the concentration of NH_4^+ in the solution was determined by the colourimetry method as previously described.

2.2. Wastewater sample from STP

The wastewater sample used in this study was obtained from "La Almozara" STP in Zaragoza (Spain) and it was taken after passing through the last system of treatment (secondary) and before discharging into the Ebro river. The concentrations of main cations and NH_4^+ in the wastewater were determined by ICP-OES and colourimetry, respectively [21].

Treatment experiments were carried out in two ways, using a batch process through the addition of fine ZM to the wastewater, and through a continuous process, allowing the wastewater to flow through a fixed bed of coarse ZM.

Removal of NH_4^+ with ZM can be affected by presence of other cations in the wastewater (competition for cation exchange sites). Therefore, it is important to know the chemical characteristics of the wastewater before any attempt can be made to examine the capacity of zeolites to remove NH_4^+ from it. Final NH_4^+ concentration in the depurated wastewater was determined by colourimetry as referred previously [21].

2.3. Batch adsorption study

NH_4^+ uptake experiments were carried out by mixing 20 ml of waste solution with fine NaP1, K-F and K-Phillipsite/K-Chabazite materials with continuous stirring at room temperature for 30 min (time calculated previously as enough to complete cation exchange). In order to reduce NH_4^+ concentration as much as possible, each ZM was dosed considering different ratios of meq of exchangeable cation in ZM (S) to meq of cations in wastewater (L), with S/L = 0.5:1, 1:1, 2:1, 3:1 and 4:1. In this way, the ZM doses used in experiments were continuously increased until NH_4^+ concentration remained constant after treatment with two consecutive doses, those similar concentrations meaning that maximum NH_4^+ removal had been achieved. When cation exchange was considered to be finished, ZM was separated by filtration (pore of paper <0.45 μm) and NH_4^+ not retained on that material was determined in filtrate as has pointed out before.

2.4. Column study

As it has been noted before, NH_4^+ uptake experiments were carried out in a glass column with 1 cm inner diameter by allowing 50 ml of wastewater to flow through a packed bed of each coarse ZM (1 g ZM represents about 2 cm bed height) at room temperature, using a flow rate of 0.35 ml/min, which was deduced from previous studies to be the minimum flow needed to achieve the best cation exchange. Flows under 0.35 ml/min do not improve cation exchange. Only two ratios S/L were used, 1:1 and 2:1, in order to prevent decreased flow through the column. This phenomenon could occur if small amounts of zeolitic powder (≤0.2 mm) surrounding the coarse granules, but easily released, were to separate from the granule and become compacted onto the packed bed filter. This would hinder correct column operation. NH_4^+ content in the depurated wastewater was determined once it had left the column.

3. Results and discussion

3.1. Zeolitic materials

Values of CEC obtained for the two fractions of the ZM studied are shown in Table 1. Considering that repeatability for determination of CEC as described in Section 2.1 was ≤0.02 meq/g, according to experimental measurements carried out on different ZM in a previous work [20], differences in CEC showed in Table 1 can be considered meaningful. CEC for fine fractions of NaP1 and K-F materials being higher than that of coarse, suggest that fine fractions for those materials present higher content in zeolite. CEC for ZM are proportional to the concentration of zeolites with cation exchange properties present in ZM because they are the only component in ZM with capacity for cation exchange as it has been noted in a previous publication [20].